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## COMMUNICATIONS TO THE EDITOR

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### THE GELATION OF MAGNESIUM SILICATE SUSPENSIONS BY CARBON DIOXIDE AND OTHER AGENTS

Sir:

Several months ago, in the course of some experiments with precipitated and washed silicates of magnesium, we observed that the passage of carbon dioxide through fluid suspensions of these silicates in water soon caused the suspensions to "set up" or gel. The resulting gels were found to be thixotropic,<sup>1</sup> that is, capable of an isothermal, reversible sol-gel transformation, being liquefied on shaking and setting spontaneously.<sup>2</sup>

Thus, within one and one-half minutes following the treatment of 10 cc. of an 8.1% suspension of MgO, 1.6SiO<sub>2</sub> (pH 9.3) with a rapid stream of carbon dioxide for one-half minute, the originally fluid suspension had "set up," so that the test-tube (16 by 150 mm.) containing it could be inverted without flow taking place. Vigorous shaking of the solidified material (pH 7.2) produced liquefaction; upon standing undisturbed, spontaneous reversion to the gel state occurred in less than a minute. The process could be repeated indefinitely.

Similar observations were made with suspensions of MgO, 1.1SiO<sub>2</sub> (6.1%) and MgO, 3.6SiO<sub>2</sub> (8.4%).

The magnesium silicates were prepared by slowly adding water solutions of various silicates of sodium to water solutions of magnesium sulfate,<sup>3</sup> with vigorous stirring. The resulting

(1) Cf. Freundlich and Gillings, *J. Chem. Soc.*, 546 (1938); MacArthur, U. S. Patent 2,168,228 (1939).

(2) For an excellent summary of our knowledge of the phenomenon of thixotropy, see Freundlich, "Thixotropy," No. 267 of "Actualités scientifiques et industrielles," Hermann et Cie, Paris, 1935.

(3) The proportions, concentrations, and composition of the reactants were:

MgSO <sub>4</sub> ·7H <sub>2</sub> O	Sodium silicate	Magnesium silicate <sup>5</sup>
3.22 moles (0.13 M soln.)	3.25 moles Na <sub>2</sub> O, 1.00 SiO <sub>2</sub> (1.6 M soln.)	MgO, 1.1SiO <sub>2</sub>
3.44 moles (0.13 M soln.)	3.49 moles Na <sub>2</sub> O, 1.48 SiO <sub>2</sub> (1.1 M soln.)	MgO, 1.6SiO <sub>2</sub>
2.71 moles (0.13 M soln.)	2.77 moles Na <sub>2</sub> O, 3.27 SiO <sub>2</sub> <sup>6</sup> (0.5 M soln.)	MgO, 3.6SiO <sub>2</sub>

<sup>5</sup> "E" Brand sodium silicate, of the Philadelphia Quartz Company from which the other sodium silicates were prepared by the addition of the requisite amounts of sodium hydroxide.

(4) Washing was continued at least until portions of the filtrates

precipitates were collected and washed in a filter press,<sup>4</sup> and portions of the wet products<sup>5</sup> were ground with water for a few minutes in a mortar to yield the rather coarse suspensions which, after vigorous shaking, were employed in the above experiments.

More recently, we found that hydrochloric acid, sulfuric acid, or acetic acid, in small amounts, could be substituted for carbon dioxide in the above experiments, to give similar results. Thus, following the addition of 0.4 cc. of *N* hydrochloric acid (0.0004 mole) to 10 cc. of an 8.1% suspension of MgO, 1.6SiO<sub>2</sub> (0.006 mole; pH 9.3), contained in a 16 by 150-mm. test-tube, gelation occurred in about half a minute. The setting time of the thixotropic product (pH 7.7) was less than fifteen seconds. Further work along these lines is in progress.

Aside from its scientific interest, the present phenomenon may find some application in the arts.<sup>6</sup>

showed no tests (or only faint tests) for sodium (with uranyl zinc acetate) and sulfate (with BaCl<sub>2</sub>, HCl).

(5) Complete analyses of the products, first dried (55°) and pulverized, were made, with the following results:

SiO <sub>2</sub> , %	44.35	52.58	67.05
MgO, %	27.90	22.20	12.49
H <sub>2</sub> O, %	27.14	24.05	18.67
R <sub>2</sub> O <sub>3</sub> , %	0.46	0.42	0.34
CaO, %	.26	.18	.12
Na <sub>2</sub> O, %	.24	.35	1.21
SO <sub>4</sub> , %	< .01	None	< 0.01
	100.35	99.78	99.88
Molecular ratio, MgO:SiO <sub>2</sub> ,	1:1.07	1:1.59	1:3.60

(6) Cf. Mutch, *Brit. Med. J.*, 1, 143, 205, 254 (1936); Levin and co-workers, *Rev. Gastroenterol.*, 6, 299 (1939); Hauser and Le Beau, *J. Phys. Chem.*, 42, 961 (1938); 43, 1037 (1939).

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### REDUCTION OVER A RANEY CATALYST OF THE ESTERS OF $\alpha$ -AMINO ACIDS TO CORRESPONDING ALKAMINES

Sir:

P. L. de Benneville and Ralph Connor report [THIS JOURNAL, 62, 283 (1940)] on the reduction of an ester to an alcoholic group by the aid of a nickel catalyst. This is regarded by the authors as the first instance of such a reaction.